Separation and Purification Technology 201 (2018) 318–326

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Separation of transition metals from rare earths by non-aqueous solvent extraction from ethylene glycol solutions using Aliquat 336

Zheng Li, Xiaohua Li, Stijn Raiguel, Koen Binnemans*

KU Leuven, Department of Chemistry, Celestijnenlaan 200 F, B-3001 Heverlee, Belgium

ARTICLE INFO

Keywords:
Non-aqueous solvent extraction
Solvometallurgy
Salting-out effect
Transition metals
Rare-earth elements

ABSTRACT

Solvent extraction is a widely used separation technique in extractive metallurgy. A conventional solvent extraction system consists of an aqueous phase and an immiscible organic phase. In this work, we show that replacement of water by a polar organic solvent can lead to superior metal separations. Cobalt(II) and samarium (III) chlorides dissolved in water and ethylene glycol (EG), respectively, with LiCl as chloride source, were extracted by Aliquat 336 diluted in toluene. Both cobalt and samarium were extracted from the aqueous solutions, but cobalt was extracted more efficiently from the ethylene glycol solutions than from the aqueous solutions, whereas samarium was not extracted at all from the ethylene glycol solutions. As a result, cobalt and samarium could be separated completely in a single extraction step from ethylene glycol solutions. The mechanisms of cobalt extraction by Aliquat 336 from the ethylene glycol and aqueous solutions were found to be similar, as validated by slope analysis and UV–VIS absorption spectroscopy. Samarium was extracted from the aqueous solution through the salting-out effect of LiCl. Interestingly, LiCl has a much lower salting-out effect for samarium in ethylene glycol than in water due to the lower dielectric constant of ethylene glycol and the lower solubility of LiCl in ethylene glycol. Consequently, samarium is not salted out from ethylene glycol, leading to a very efficient separation of cobalt and samarium. This separation effect can also be applied to the separation of other transition metal and rare-earth metal pairs, including iron/neodymium and zinc/europium.

1. Introduction

Solvent extraction (SX), also known as liquid-liquid extraction, is a separation technique widely used for separation and purification of metals [1]. It is obvious from its name that solvent extraction consists of two liquid phases. In general, one is an aqueous phase (more polar) containing the metals to be separated and the other is an immiscible organic phase (less polar) containing an extractant. In addition to the extractant, the less polar phase can contain a variety of components [2]: (1) a diluent is used to reduce the viscosity of the extractant and it has also an effect on the extraction efficiencies and hence on the selectivity of the extraction process; (2) in some cases, modifiers are used to prevent formation of a third phase; (3) a second and even a third extractant can be added as synergists to enhance the selectivity. The complexes formed by the metal cation and the extractant are hydrophobic and stay in the less polar phase. Because of the presence of several components in the less polar phase, extensive studies on various aspects of the less polar phase of the solvent extraction systems have been performed. On the other hand, only little attention has been paid to the other phase, which by default is the aqueous phase.

However, the more polar phase does not necessarily need to be water; any solvent pair that forms two immiscible phases can be used for solvent extraction. There exist plenty of studies on liquid-liquid equilibria of multiple non-electrolyte components not involving water [3–8], but studies on solvent extraction of metals without an aqueous phase are scarce. Larsen and Trevorrow developed a non-aqueous system containing isoamyl ether and acetonitrile as two immiscible phases and investigated the distributions of $ZrCl_4$ and $HfCl_4$ [9]. This study is perhaps the first example of a non-aqueous solvent extraction system for metals reported in the literature. Latimer investigated the distributions of a number of metal salts between diethyl ether and ethanolamine, formamide and adiponitrile. Except for $SnCl_4$ which showed some preference for the ether phase, all other salts distributed preferentially (> 90%) to the non-ether phase [10]. Florence and Farrar studied the extraction of $NiCl_2$ by Alamine 336 from both aqueous solutions and methanolic solutions with assistance of halide salts. It was found that the concentration of halide salt necessary for the extraction of Ni(II) is much lower in the methanolic solution than in the aqueous solution [11]. In a follow-up study, Mn(II), Cr(III) and Th(IV) were also found to be more readily extracted from the methanolic

* Corresponding author.
E-mail address: Koen.Binnemans@kuleuven.be (K. Binnemans).

https://doi.org/10.1016/j.seppur.2018.03.022
Received 20 October 2017; Received in revised form 7 March 2018; Accepted 12 March 2018
Available online 14 March 2018

solution by Alamine 336 than from the aqueous solution [12]. It was proposed that water activity plays an important role in the extraction because the conversion of the octahedral $[Ni(H_2O)_6]^{2+}$ to the tetrahedral $[NiCl_4]^{2-}$ is favored if the water activity is low. A low water activity can be achieved by either using high chloride salt concentration (which also raises the chloride activity) or using non-aqueous solvents. Burns and Cattrall characterized the copper complexes in benzene formed by the extraction of $CuCl_2$ by bis(3,5,5-trimethylhexyl)ammonium chloride from methanolic solutions containing LiCl [13]. Matasui et al. studied the extraction of $ZnCl_2$, $ZnBr_2$ and $CdBr_2$ by trioctylphosphine oxide (TOPO) in toluene and from ethylene glycol, and the extraction of $ZnCl_2$ by TOPO in decaline from methanol-water mixtures [14–16]. Recently, Batchu et al. studied the extraction of rare-earth nitrates in a system consisting of Cyanex 923 in *n*-dodecane and ethylene glycol with $LiNO_3$. When compared to extraction from aqueous solutions, the light rare-earth elements were less efficiently extracted while the heavy rare-earth elements were more efficiently extracted, and the separation factors between neighboring elements were higher [17]. Extraction of rare-earth chlorides dissolved in ethylene glycol (with LiCl) by Cyanex 923 also showed better performance than the extraction from aqueous solutions [18]. Deep-eutectic solvents (DESs) were investigated for replacement of water in solvent extraction. Higher selectivities and extraction efficiencies than the analogous aqueous system were observed for the recycling of used NdFeB magnets in a solvent extraction system using DES as a polar solvent [19], while the water content was found to significantly affect the extraction of transition metals from the DES [20]. Besides interesting phenomena, these studies also show that sometimes better separations can be obtained using non-aqueous solvent extraction. Recently, the concept of solvometallurgy, a metallurgical methodology complementary to hydrometallurgy and pyrometallurgy, was illustrated by Binnemans and Jones, with non-aqueous solvent extraction being a key part of this approach [21]. In solvometallurgy, the aqueous phase of a hydrometallurgical process is replaced by a non-aqueous phase. It must be emphasized that “non-aqueous” does not mean “anhydrous”, but rather having an organic solvent as the main component of the polar phase. This is a good opportunity to pay more attention to the role of the more polar phase in the solvent extraction process, which has largely been overlooked so far. We can not only replace water by polar organic solvents, but also add modifiers and synergists to the more polar phase, thus to provide the solvent extraction systems with more flexibility and potentially higher selectivity.

In this paper, we show that a non-aqueous solvent extraction system consisting of the basic extractant Aliquat 336 in toluene as the less polar phase and ethylene glycol (EG) with LiCl as the more polar phase is superior to the corresponding conventional solvent extraction system with an aqueous phase for the separations of transition metals and rare-earth elements. These separations are important for the recycling and purification of rare earths [22,23]. The extractant Aliquat 336 is often used for extraction of both transition metals and rare earths, either in its chloride form or nitrate form [24–29]. It is a mixture of tri-$C_{8\text{-}10}$-alkylmethylammonium chloride with the C_8 compound trioctylmethylammonium chloride dominating. The structures of ethylene glycol and the main component of Aliquat 336 are shown in Fig. 1.

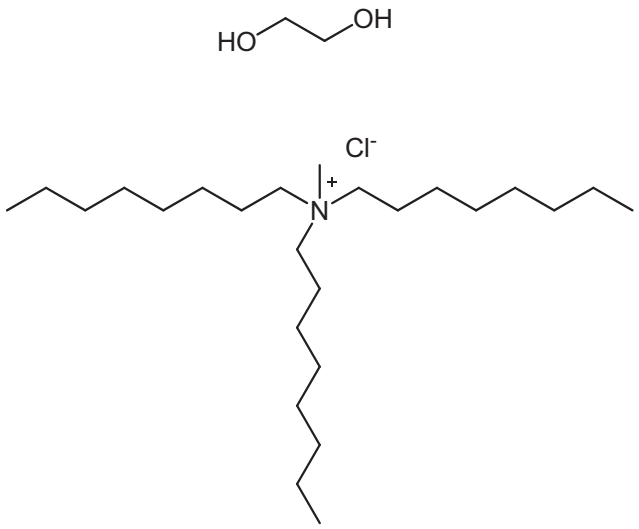

Fig. 1. Structures of ethylene glycol (top) and the main component of Aliquat 336 (bottom).

2. Experiments

2.1. Chemicals

$CoCl_2{\cdot}6H_2O$ (analytical grade), $FeCl_3$ (98%), $EuCl_3{\cdot}6H_2O$ (99.99%), ethylene glycol (99.9%) and *N,N*-dimethylformamide (DMF, 99.5%) were purchased from Acros Organics (Geel, Belgium); $NiCl_2{\cdot}6H_2O$ (97%) and Ga standard (1000 ± 10 mg/L) were purchased from ChemLab (Zedelgem, Belgium); Aliquat® 336 (~90%) and acetonitrile-d_3 (99.9%) were obtained from Sigma–Aldrich (Diegem, Belgium); $ZnCl_2$ (98%) was purchased from BDH Laboratory Supplier (Poole, UK); $LaCl_3{\cdot}7H_2O$ (99.99%) was obtained from Alfa Aesar (Karlsruhe Germany); ethanol (99.99%) and LiCl (analytical reagent grade) were supplied by Fisher Chemical (Loughborough, UK); $SmCl_3{\cdot}6H_2O$ (99.9%) and $NdCl_3{\cdot}6H_2O$ (99.9%) were obtained from Strem Chemicals (Newburyport, USA); toluene (99.5%) was purchased from VWR Chemicals (Fontenay-sous-Bois, France). A silicone solution in isopropanol for the treatment of the TXRF quartz glass carriers was obtained from SERVA Electrophoresis GmbH (Heidelberg, Germany). Milli-Q water (18.2 MΩ cm at 25 °C) was used to prepare the aqueous solutions. All chemical were used as received, without any further purification.

2.2. Experimental methods

2.2.1. Solubility experiments

Two sets of solubility experiments were conducted to investigate the effect of Aliquat 336 and LiCl, respectively, on the mutual solubility of toluene and ethylene glycol (EG). LiCl was chosen as the salting-out agent because it is the chloride salt with the highest solubility in EG. In the first set of experiments, 4.0 mL of toluene and 4.0 mL of EG were equilibrated with each other, with addition of volumes of Aliquat 336 varying from 0 mL to 8.0 mL. After shaking for 20 min at 450 rpm using a Wrist-Action® Shaker (Burrell Scientific), samples were centrifuged at 3500 rpm for 5 min. Samples in both phases were measured by ^{1}H NMR spectroscopy (400 MHz), the composition of the samples was used to calculate the mutual solubilities of the two solvents. In the second experimental set, 5 mL of 50 vol% Aliquat 336 in toluene was contacted with 5 mL of EG containing LiCl varying from 0 to 4.0 M. The compositions of the toluene-rich phase was directly determined by ^{1}H NMR, while the EG phase was diluted by DMF, which was used as a reference to determine the composition. Acetonitrile-d_3 was used as solvent for all the NMR measurements.

The solubility of $CoCl_2$ in EG was determined. An aliquot of 4.0 g $CoCl_2{\cdot}6H_2O$ was weighed in a 20 mL glass vial and transformed to anhydrous $CoCl_2$ by a heat gun. The loss of water was confirmed by weighing the dry $CoCl_2$. A 3 mL sample of EG was added to the dry $CoCl_2$ and shaken in a water bath at 25 °C for 12 h, followed by centrifuging for 2 min. The cobalt concentration in the saturated solution was measured by TXRF. The experiment was carried out in triplicate.

2.2.2. Extraction

For the extraction isotherm, 1.0 M Aliquat 336 in toluene was pre-equilibrated with water and EG, respectively, prior to extraction.

Because of extraction of water and EG by Aliquat 336, the actual concentrations were about 0.89 M and 0.75 M, respectively. The aqueous and the EG solutions containing 5.0 g/L Co(II), 1.5 g/L Sm(III) and various concentrations of LiCl were prepared from stock solutions, which were made by dissolving chloride salts in the corresponding solvents. For the solvent extraction from the aqueous solutions, 5 mL of each phase was equilibrated with each other in a 15 mL centrifuge tube by shaking at 450 rpm in a Wrist-Action® Shaker for 20 min, followed by centrifugation at 3500 rpm for 5 min, although the phase separation was also quite fast by gravity settling. To equalize the amount of the Aliquat 336 for the aqueous solvent extraction and the non-aqueous solvent extraction, a phase ratio of 1.18:1 (5.9 mL:5.0 mL) was used for the extraction from the EG solution. Here the phase ratio means the ratio of the volume of the less polar phase to the volume of the more polar phase. For the studies on the effect of Aliquat 336 concentrations, a phase ratio of 1:1 (5.0 mL for each phase) was used. The procedures were the same for all the solvent extraction experiments, as described for the aqueous solvent extraction. All experiments were carried out at room temperature.

The distribution ratio D, extraction percentage E% and separation factor α are defined in Eqs. (1)–(3).

$$D = \frac{c_{lp}}{c_{mp}} \tag{1}$$

$$E\% = \frac{c_{lp} \cdot V_{lp}}{c_{lp} \cdot V_{lp} + c_{mp} \cdot V_{mp}} \times 100\% \tag{2}$$

$$\alpha = \frac{D_A}{D_B} \tag{3}$$

where c_{lp} and c_{mp}, V_{lp} and V_{mp} are concentrations and volumes in the less polar phase and the more polar phase, respectively; D_A and D_B are the distribution ratios of metals *A* and *B,* respectively.

2.2.3. Stripping

5.0 g/L Co(II) and 1.5 g/L Sm(III) were loaded from the EG solution with 3.0 M LiCl to the toluene phase (0.75 M Aliquat 336). The loaded phase was stripped by pure EG with phase ratios of 1:1 to 1:4. For the case of phase ratio 1:1, a second stripping was also conducted with fresh EG.

2.2.4. Kinetics

The less polar phase consisted of 0.40 M Aliquat 336 in toluene and was pre-equilibrated with EG and water, respectively. The EG feed solution contained 6.0 g/L Co(II), 1.8 g/L Sm(III) and 3.5 M LiCl. The aqueous feed solution contained 6.0 g/L Co(II), 1.8 g/L Sm(III) and 5.0 M LiCl. An aliquot of 50 mL of the less polar phase was contacted with 50 mL of the EG solution or 50 mL of the aqueous solution, in a 250 mL beaker with magnetic stirring at 600 rpm. As soon as the two phases had been contacted, the time measurement was started and a 0.2 mL sample of the top phase (toluene phase) was taken out consecutively at given time intervals and measured.

2.3. Instrumentation and analytical methods

^{1}H NMR spectra were recorded on a Bruker Avance 400 spectrometer operating at 400 MHz using acetonitrile-d_3 as solvent for all the samples. The metal concentrations in the less polar phase and the more polar phase were determined by a total reflection X-ray fluorescence (TXRF) spectrometer (Bruker S2 Picofox) after the samples were diluted in mixtures of ethanol and water to an appropriate concentration range [30,31]. A standard gallium solution was added to the samples during dilution as an internal standard. The UV–VIS absorption spectra were recorded by a Varian Cary 5000 spectrophotometer with a pair of quartz cuvettes of 10.0 mm path length. The water content was measured by a Karl Fischer Coulometer (Mettler-Toledo C30S).

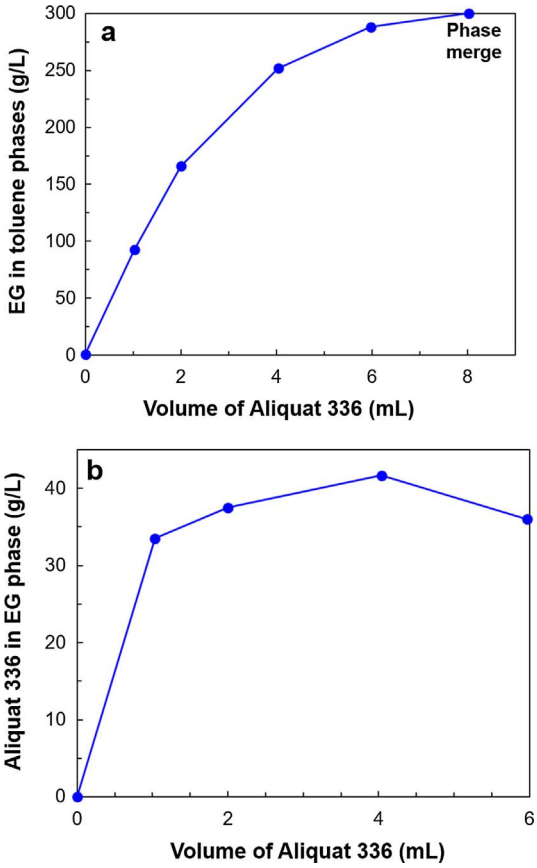

Fig. 2. Mutual solubility of toluene and EG with increasing Aliquat 336 concentration, at room temperature: (a) EG in the toluene phase; (b) Aliquat 336 in the EG phase.

3. Results and discussions

3.1. Solubility and viscosity

Toluene was found to be a good diluent for Aliquat 336, without formation of an emulsion or a third phase. Besides being readily soluble in toluene, Aliquat 336 is also miscible with EG. However, toluene and EG are mutually immiscible. At room temperature, the solubility of toluene in EG is about 25 g/L and the solubility of EG in toluene is as low as 0.91 g/L, as estimated by ^{1}H NMR spectroscopy. The concentration of Aliquat 336 in toluene largely affects the phase equilibrium. As shown in Fig. 2, upon addition of Aliquat 336 to the two-phase system initially containing 4.0 mL of toluene and 4.0 mL of EG, respectively, the solubility of EG in the toluene phase increased from 0.91 g/L in the absence of Aliquat 336 to 288 g/L at 6.0 mL of Aliquat 336 and the two phases merged into one phase at 8.0 mL of Aliquat 336. Interestingly, the amount of Aliquat 336 in EG remained constant at a value of about 36 g/L. With the addition of LiCl to EG for systems containing 5.0 mL of EG solution and 5.0 mL of 50 vol% Aliquat 336 in toluene, the solubility of EG in the toluene phase decreased from 268 g/L at 0 M LiCl to 142 g/L at 4.0 M LiCl, which is a decrease of almost 50% (Fig. 3). Similarly, the solubility of toluene and Aliquat 336 in the EG solution also decreased, from 22.1 g/L and 42.2 g/L, respectively, at 0 M LiCl to 4.6 g/L and 1.8 g/L at 3.5 M LiCl, and further to 4.1 g/L and 1.5 g/L at 4.0 M LiCl (4.0 M is the LiCl saturation concentration in EG at room temperature). In this non-aqueous solvent extraction system, the loss of toluene and Aliquat 336 to the EG phase is low at high LiCl concentrations, but EG is quite soluble in the toluene phase when the toluene phase contains high concentrations of Aliquat 336. Fortunately, EG in the toluene phase does not show negative effects on the extraction and the role of the dissolved EG is similar to that of a diluent.

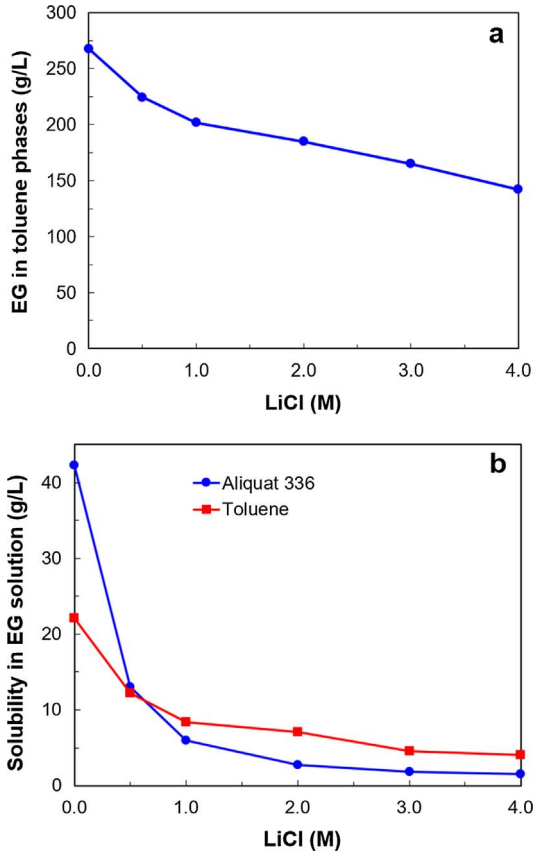

Fig. 3. Effect of LiCl concentration on the mutual solubility, at room temperature: (a) solubility of EG in the toluene phase; (b) solubility of toluene and Aliquat 336 in the EG phase.

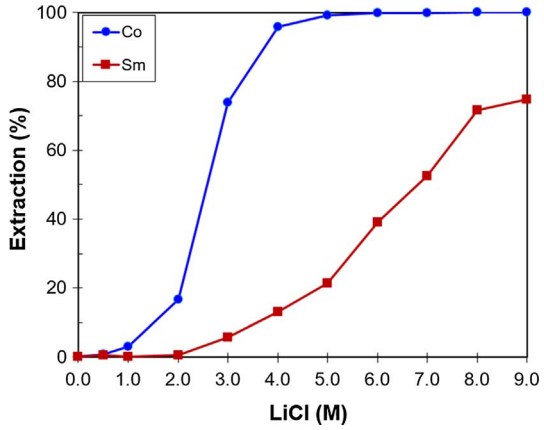

Fig. 4. Extraction of Co(II) and Sm(III) (5.0 g/L Co and 1.5 g/L Sm in water) by 0.89 M Aliquat 336 in toluene. The phase ratio was 5.0 mL:5.0 mL.

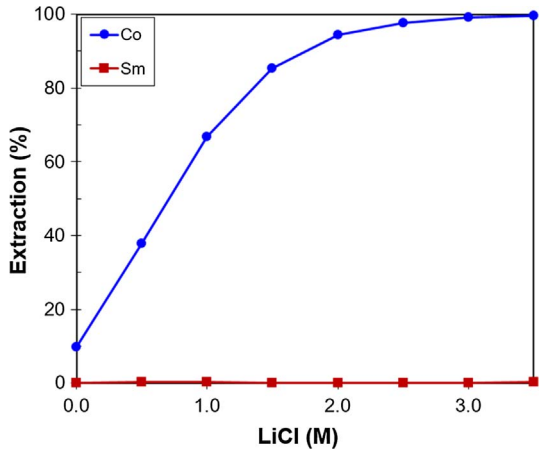

Fig. 5. Extraction of Co(II) and Sm(III) (5.0 g/L Co and 1.5 g/L Sm in EG) by 0.75 M Aliquat 336 in toluene, phase ratio was 5.9 mL:5.0 mL.

The solubilities of $SmCl_3$ and $CoCl_2$ in water at room temperature are 7.0 mol/kg and 3.6 mol/kg respectively [32,33]. The solubility of $SmCl_3$ in EG is 1.91 mol/kg [34]. The solubility of $CoCl_2$ in EG at room temperature was measured to be 1.79 mol/kg. This shows that both $SmCl_3$ and $CoCl_2$ are readily soluble in both water and EG.

The viscosity of EG at 25 °C is 18 mPa·s and increases to 53 mPa·s at 2.0 M LiCl and reaches a value of 211 mPa·s at 4.0 M LiCl [18]. On the other hand, the viscosity of an aqueous LiCl solution is much lower: pure water has a viscosity of 0.89 mPa·s at 25 °C, while aqueous solutions containing 1.0, 2.0 and 4.0 M LiCl have viscosities of 1.1, 1.2 and 1.6 mPa·s, respectivly. A saturated aqueous LiCl solution (13.0 M) has a viscosity of only 12.7 mPa·s [35].

3.2. Cobalt and samarium extraction isotherms

Isotherms of Co(II) and Sm(III) extraction by water-saturated Aliquat 336 in toluene (initial Aliquat 336 concentration was 1.0 M, after water saturation it was about 0.89 M) from aqueous solution with a phase ratio of 1:1 are shown in Fig. 4. Extraction of both metals increased with an increasing LiCl concentration. At 5.0 M LiCl, 99.2% Co (II) was extracted, while 21.3% Sm(III) was extracted, and the separation factor was 462. For LiCl concentrations > 6.0 M, Co(II) extraction was almost complete (> 99.8%), but much more Sm(III) was co-extracted. The maximum extraction of Sm(III) was 74.7% at 9.0 M LiCl. 5.0 M LiCl is a proper condition for separation of Co(II) and Sm(III), but multiple stages of scrubbing would be needed because of the high co-extraction of the Sm(III).

Extraction of Co(II) and Sm(III) by Aliquat 336 in toluene (initial Aliquat 336 concentration was 1.0 M, after EG saturation the concentration was about 0.75 M) from the EG solution is very different from the aqueous system, as shown in Fig. 5. The extraction of Co(II) increased with the increasing LiCl concentration. 98.9% Co(II) was extracted at 3.0 M LiCl, which is comparable to the extraction of Co(II) at 5.0 M LiCl from the aqueous solution, indicating that less LiCl is needed for Co(II) extraction from the EG solution due to the absence of water. This phenomenon is similar to the extraction of Ni(II) by Alamine 336 from a methanolic solution [11]. Almost quantitative extraction of Co(II) (99.6%) was achieved at 3.5 M LiCl, while 6.0 M LiCl was required to achieve quantitative Co(II) extraction from the aqueous solution. More importantly, Sm(III) was not extracted at all (below the detection limit of TXRF (< 0.1 mg/L)) from the EG solutions. Therefore, complete separation of Co(II) and Sm(III) can be achieved in a single extraction step with LiCl concentrations ≥ 3.5 M. $SmCl_3$ in the raffinate could not be precipitated by oxalic acid due to the high solubility of samarium(III) oxalate in EG. This is opposite to aqueous systems, where it is common practice to recover the rare earths from solution by precipitation as their oxalates. However, $SmCl_3$ can be extracted directly from the LiCl-containing EG solution by Cyanex 923 [18]. Then the LiCl-containing EG solution can be reused for a next solvent extraction step. The $SmCl_3$ can be stripped from the loaded Cyanex 923 phase by water.

Fig. 6 shows a picture of the extraction systems after equilibration. The two phases for both extraction systems were clear. No emulsion was formed. The extraction of cobalt(II) from the aqueous solution with 3.0 M LiCl was about 73.9%, the remaining cobalt(II) was in the form of $[Co(H_2O)_6]^{2+}$ and showed a faint pink color. By contrast, the extraction efficiency of cobalt(II) from the EG solution with 3.0 M LiCl was over 99%. Therefore the lower EG phase was colorless because of the low

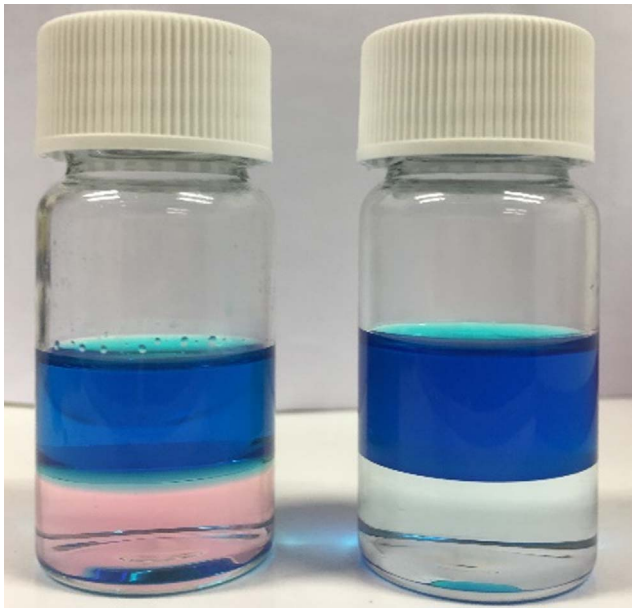

Fig. 6. Extraction of cobalt(II) from the aqueous solution (left) and the EG solution (right). 5.0 g/L Co and 1.5 g/L Sm with 3.0 M LiCl in the water/EG phase.

remaining cobalt concentration. The phase disengagement was fast for both systems: clear interfaces were observed within about five minutes after stopping shaking. The viscosity of the EG solution was higher than that of the aqueous solution, but the density difference of the two phases in the EG system was larger, and as a results, the phase disengagement times of the two systems were comparable.

3.3. Extraction mechanism

Extraction of Co(II) by Aliquat 336 from an aqueous chloride solution has been proposed as an anion exchange reaction, as shown in eq (4) [36]:

$$CoCl_4^{2-} + 2\overline{R_3R'NCl} \leftrightarrows \overline{(R_3R'N)_2CoCl_4} + 2Cl^- \quad (4)$$

The bar indicates the compounds in the toluene phase. The UV–VIS absorption spectra of the loaded toluene phase in contact with the aqueous solution and the EG solution were both measured. Three representative peaks for the tetrahedral $[CoCl_4]^{2-}$ complex at wavelengths between 600 nm and 700 nm were clearly observed (Fig. 7), indicating that extraction of Co(II) from the EG solution is similar to the extraction from the aqueous solution.

Sm(III) does not form complexes with chloride ions in aqueous solutions, even not at very high chloride concentrations, so that it cannot be extracted by Aliquat 336 through an anion exchange mechanism. An Extended X-ray Absorption Fine Structure (EXAFS) study has shown that Sm(III) stays in Aliquat 336 in the form of $[Sm(H_2O)_9]^{3+}$ [37]. Based on this result, we propose that Sm(III) is extracted by Aliquat 336 through a salting-out effect. This is consistent with the fact that more Sm(III) is extracted (salted-out) at higher LiCl concentrations in the aqueous solution. Much earlier, Seeley and Crouse investigated the extraction of 63 metals by amines with LiCl concentrations varying from 0.5 to 10 M and they found that the extraction of most metals from LiCl solutions was more efficient than from HCl solutions having the same total chloride concentration [38], indicating the salting-out effect of LiCl.

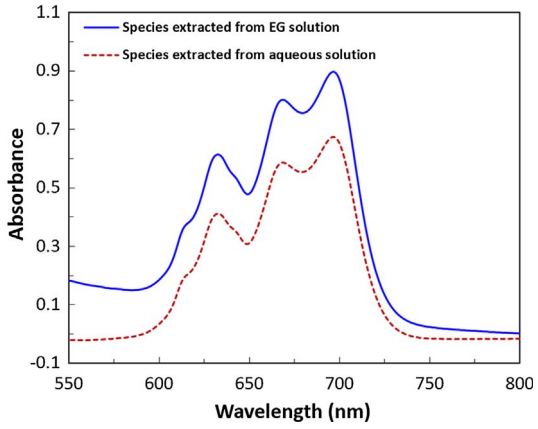

Fig. 7. UV–VIS absorption spectra of the metal complexes extracted by Aliquat 336 from the aqueous and the EG solutions.

EXAFS studies for $Nd(NO_3)_3$ in EG have shown the coordination of $[Nd(H_2O)_6(EG)_3]^{3+}$ (water is introduced by hydration of the neodymium nitrate) [17]. Whereas, $YbCl_3$ in EG was reported to be $[Yb(H_2O)(EG)_4]^{3+}$ with four bidentate EG molecules. The difference between the coordination structures of Nd(III) and Yb(III) in EG was attributed to the different water content involved in the extraction systems [18]. Considering the chemical similarities among Sm(III), Nd(III) and Yb(III), both $[Sm(H_2O)_6(EG)_3]^{3+}$ and $[Sm(H_2O)(EG)_4]^{3+}$ are possible for Sm(III) in EG, depending on the water content. Sm(III) is not salted out to the Aliquat 336/toluene phase for three reasons: (1) the dielectric constant of EG (41 at 25 °C and 1×10^5 Hz) is much lower than that of water (78.2 at 25 °C and 1×10^5 Hz) [39], the lower dielectric constant of EG weakens the dissociation of salts, leading to a lower electrical conductivity and consequently a weaker salting-out effect; (2) the maximum concentration of LiCl used in EG for the non-aqueous solvent extraction was 3.5 M, which might be too low to display any salting-out effect; (3) water-saturated Aliquat 336 (0.89 M) solution contains about 12.4 wt% water as determined by Karl Fischer titration, which means that this solution is more hydrophilic than the Aliquat 336 solution not contacted with water, which contains only 1.7 wt% water. Solutions of higher hydrophilicity are more capable to accommodate the hydrated hydrophilic $[Sm(H_2O)_9]^{3+}$ complex.

To understand the effect of water on the extraction of Co(II), UV–VIS absorption spectra were recorded for 0.25 M $CoCl_2$ with 1.0 M LiCl in 100% water, a mixture of 20 vol% water and 80 vol% EG and 100% EG. The spectra are shown in Fig. 8 along with photographs of the solutions. In the EG solution, $CoCl_2$ displayed a blue color which indicates the existence of the $[CoCl_4]^{2-}$ complex. The formation of the $[CoCl_4]^{2-}$ complex in EG was validated by the UV–VIS spectrum of the blue solid line in Fig. 8. The three peaks in the 600–700 nm spectral region are typical for the tetrahedral $[CoCl_4]^{2-}$ complex [40]. With addition of 20 vol% water, the color converted to pink with a slightly bluish shade, while the intensity of the absorption bands of the $[CoCl_4]^{2-}$ complex largely decreased. When pure water was used, the color of the solution was completely pink and the characteristic absorption bands of the $[CoCl_4]^{2-}$ complex disappeared in the spectrum. The color of the three $CoCl_2$ solutions and their UV–VIS spectra show that the $[CoCl_4]^{2-}$ is more readily formed in the EG solution than in water. This phenomenon explains why $CoCl_2$ is extracted more efficiently by Aliquat 336 from the EG solution than from the aqueous solution. The conversion of $[Co(H_2O)_6]^{2+}$ to $[CoCl_4]^{2-}$ is favored at low water activity, similar to the extraction of Ni(II) from a methanolic solution, as reported by Florence and Farrar [11]. The absorption band at 515 nm in 100% water represents the octahedral $[Co(H_2O)_6]^{2+}$ complex [41]. It shifted to 523 nm in 80 vol% EG solution and to 533 nm in 100% EG solution, indicating the involvement of EG in the first coordination sphere. A possible stoichiometry is $[Co(H_2O)_x(EG)_{6-x}]^{2+}$.

3.4. Effect of extractant concentration and kinetics

The effect of the Aliquat 336 concentration on the extraction was investigated (Fig. 9). As expected, the extraction of Co(II) increased

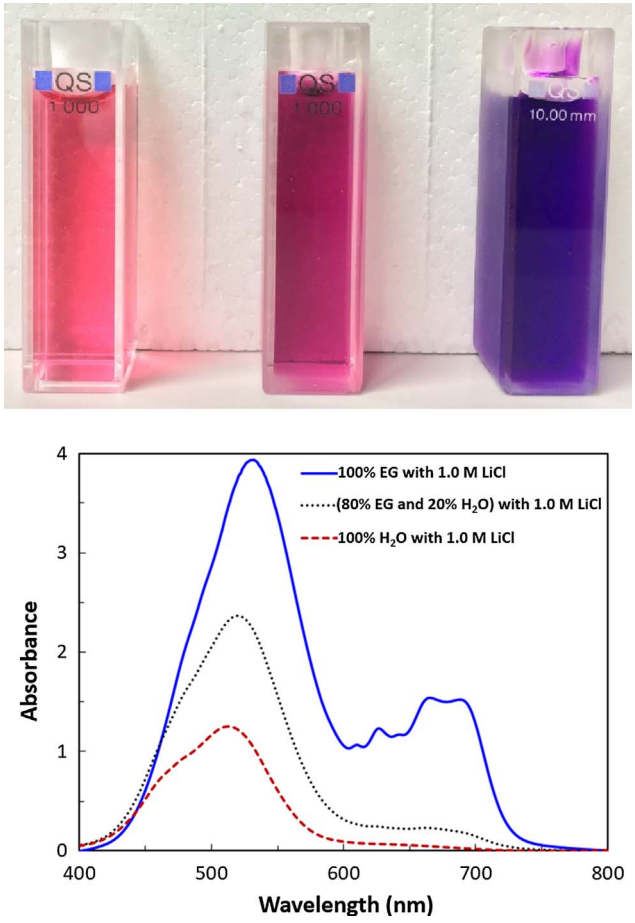

Fig. 8. Top: Solutions of 0.25 M $CoCl_2$ and 1.0 M LiCl in 100% water (left), 20 vol% water + 80 vol% EG (middle) and 100% EG (right); Bottom: Corresponding UV–VIS absorption spectra of the three solutions.

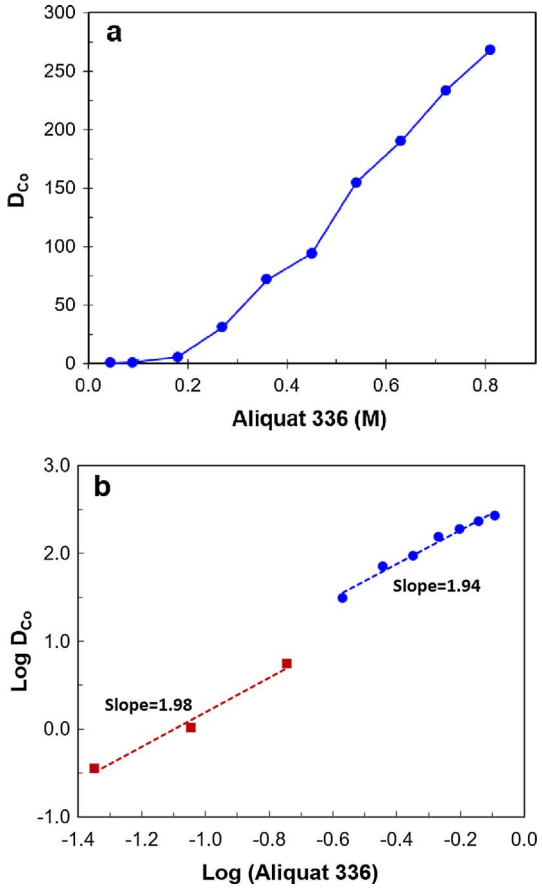

Fig. 9. Effect of extractant concentration. More polar phase: 5.0 g/L Co and 1.5 g/L Sm with 3.5 M LiCl; Less polar phase: various concentrations of Aliquat 336 in toluene.

with increasing concentrations of Aliquat 336. When the Aliquat 336 concentration was 0.09 M, the distribution ratio was 1.02 (51% extraction). At 0.18 M, the distribution ratio reached a value of 5.49 (85% extraction). From 0.18 M to 0.27 M, the distribution ratio D jumped to a value of 30.9. The jump in distribution ratio might be due to the fact that 0.27 M surpasses the stoichiometric ratio of Aliquat 336 to Co(II) for 5.0 g/L Co(II) (0.085 M) as is shown in eq. (4), *i.e.*, the molarity of Aliquat 336 concentration was more than two times higher than that of Co(II). The small jump in distribution ratio may also be caused by experimental errors because the tested concentrations cover a wide range. About 99% (D = 94) of Co(II) was extracted at 0.45 M, and up to 99.6% (D = 268) was extracted by 0.81 M Aliquat 336. Extraction of Sm(III) could not be detected because the concentration of Sm(III) in the less polar phase was below the detection limit of TXRF. Therefore extraction of Sm(III) is not shown in Fig. 9. Since Sm(III) is not extracted, a slope analysis for Co(II) could be conducted (Fig. 9.b). Considering that there is a jump in the distribution ratio between 0.18 M and 0.27 M, the slope was fitted separately and both lines gave slopes close to 2.0. When all the data points were fitted together, the slope was about 2.4, which is still close to 2.0, meaning that two quaternary ammonium cations bind to one $[CoCl_4]^{2-}$ anion. The slope analysis is consistent with the extraction mechanism proposed in eq. (4).

The extraction kinetics were measured for the two extraction systems (Fig. 10). Equilibrium was reached in 6 to 8 min for the extraction from the EG solution, which is quite fast. The extraction from the aqueous solution was even faster and equilibrium was reached in 3 min. The slightly slower kinetics for the extraction involving EG is due to the higher viscosity of the EG solution and hence a slower mass transfer.

3.5. Stripping

The loaded Aliquat 336 (0.75 M in toluene) with about 5.0 g/L Co (II) was stripped by pure EG with phase ratios of 1:1, 1:2, 1:3 and 1:4 (Fig. 11). The stripping percentage was 82.0% at a phase ratio of 1:1, and increased to 92.9%, 96.0% and 97.5% when the phase ratio was increased to 1:2, 1:3, and 1:4 respectively. When the loaded phase was stripped twice by EG at a phase ratio 1:1, 98.4% of Co(II) was stripped. Therefore, the loaded Co(II) can be efficiently stripped with pure EG. The $CoCl_2$ stripped to EG can be further precipitated to produce cobalt salt, and it is also possible to directly get cobalt metal through electrodeposition in EG [42,43]. After removal of $CoCl_2$, the EG solvent can be reused for stripping.

3.6. Separation of transition metals from rare earth elements

Further separations were tested for four pairs of transition metals and rare-earth elements, with aqueous and EG feed solutions containing 1.0 g/L of each metal: Co(II)/Sm(III) (for recycling of metals from SmCo magnets), Ni(II)/La(III) (for recycling of metals from nickel metal hydride batteries), Fe(III)/Nd(III) (for recycling of metals from NdFeB magnets) and Zn(II)/Eu(III) (relevant when europium is separated from a mixture of rare earths by reduction of Eu(III) to Eu(II) by zinc powder or zinc amalgam, followed by re-oxidation of Eu(II) to Eu(III) in an extraction process to separate europium from yttrium) [22,44]. The less polar phase was 1.0 M Aliquat 336 in toluene pre-saturated with either water or EG, the phase ratio was 1:1 for aqueous solvent extraction and 1.18:1 for extraction from EG solution (Figs. 12 and 13).

For the extraction from the aqueous solution (Fig. 12), Zn(II) had the highest affinity to Aliquat 336 and could be extracted up to 99.5%

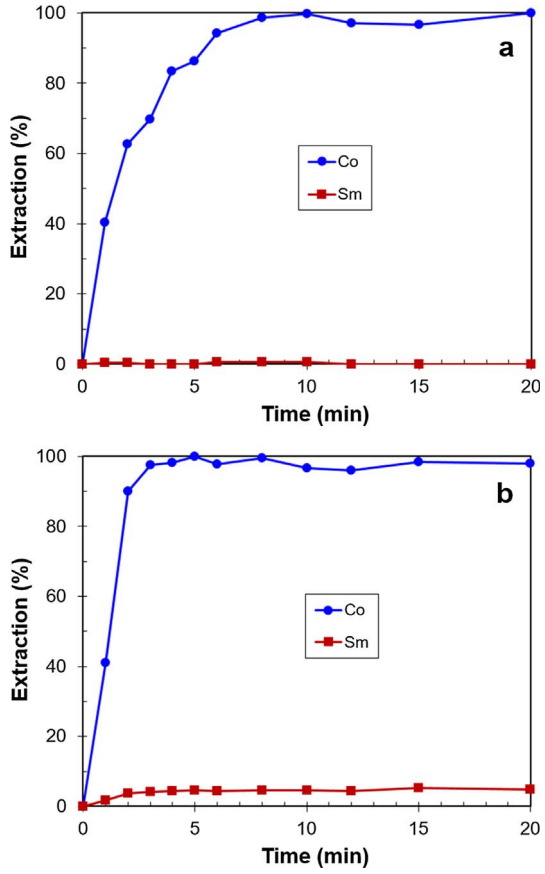

Fig. 10. Kinetics of extraction from the EG solution: (a)more polar phase is 6.0 g/L Co and 1.8 g/L Sm with 3.5 M LiCl; and from the aqueous solution (b) more polar phase is 6.0 g/L Co and 1.8 g/L Sm with 5.0 M LiCl. The less polar phase is 0.40 M Aliquat 336 in toluene pre-equilibrated with EG and water, respectively.

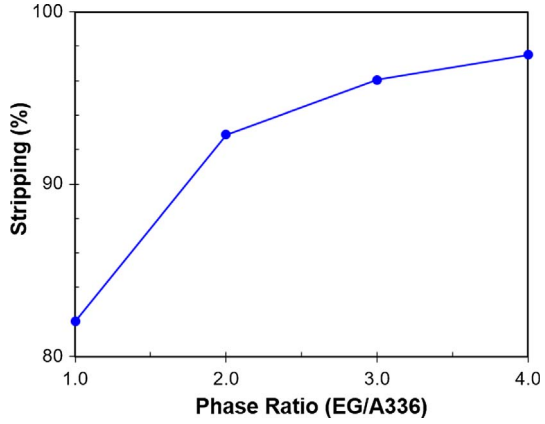

Fig. 11. Stripping of cobalt(II) chloride by EG at various phase ratios.

without addition of LiCl. Fe(III) could also be extracted easily, with 46.4% and 99.3% extraction at 0 M LiCl and 1.0 M LiCl respectively, complete extraction could be achieved at > 2.0 M LiCl (99.7% extraction). Extraction of Co(II) increased with an increase in LiCl concentration and is similar to the result in Fig. 4. At 5.0 M LiCl, 99.0% of Co(II) was extracted; at 6.0 M LiCl, 99.8% of Co(II) was extracted. Extraction of Ni(II) was the least efficient among the transition metals, with only 28.0% extraction at 9.0 M LiCl. This result is consistent with the study of Florence and Farrar which showed that about 20% Ni(II) was extracted with Alamine 336 at 9.0 M LiCl and quantitative extraction of Ni(II) can be achieved with 13 M LiCl [11]. Extraction of the rare-earth elements increased with increasing LiCl concentration in a

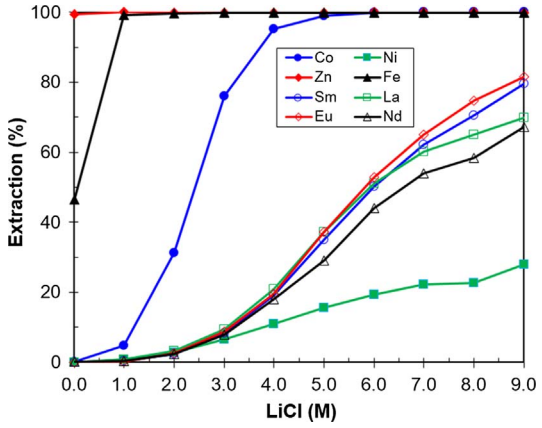

Fig. 12. Extraction of metals from aqueous solution as a function of the LiCl concentration. The less polar phase was 1.0 M Aliquat 336 in toluene saturated with water, the aqueous solution was 1.0 g/L of each metal with varying LiCl concentration.

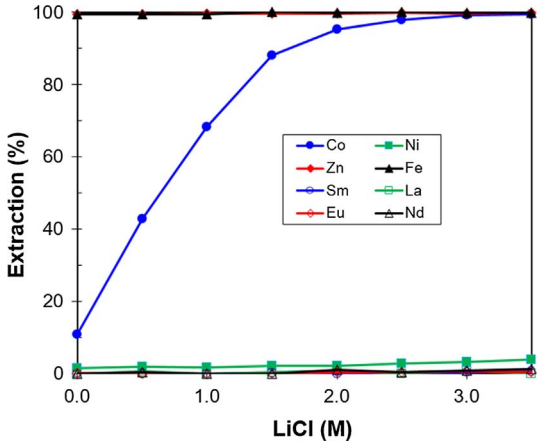

Fig. 13. Extraction of metals from the EG solution as a function of the LiCl concentration. The less polar phase was 1.0 M Aliquat 336 in toluene saturated with EG, the more polar phase was 1.0 g/L of each metal in EG with varying LiCl concentration.

similar manner and up to 69.9% La(III), 67.1% Nd(III), 79.5% Sm(III) and 81.6% Eu(III) was extracted at 9.0 M LiCl. When the LiCl concentration is low, Zn(II) and Eu(III) can be separated potentially in a single step, but the separation becomes more difficult when the concentration of chlorides is higher, due to the salting-out of Eu(III). Separation of Fe(III)/Nd(III) is more difficult than that of Zn(II)/Eu(III) and requires careful selection of chloride concentration and further scrubbing of Nd(III) would be needed. Separation of Co(II)/Sm(III) is even more difficult as discussed in Section 3.1. Separation of Ni(II)/La (III) is not feasible due to the poor affinity of Aliquat 336 for Ni(II).

In contrast to the extraction from the aqueous solutions, the non-aqueous extractions show significant improvement for the separations (Fig. 13). At any LiCl concentration investigated, the rare-earth elements were not extracted at all (the metal content in the less polar phase was below the detection limit of TXRF). Both Zn(II) and Fe(III) were extracted completely at all LiCl concentrations, indicating that complete separation of Zn(II)/Eu(III) and Fe(III)/Nd(III) can be achieved readily. Co(II) was extracted completely at 3.5 M LiCl, under which condition complete separation of Co(III)/Sm(III) could be achieved. Extraction of Ni(II) slightly increased with increasing LiCl concentrations, from 1.4% at 0 M LiCl to 4.0% at 3.5 M LiCl. Therefore, it is difficult to separate Ni(II) from La(III) using this extraction system, but separation of Co(II) and Ni(II) is feasible. At 3.0 M LiCl, 99.3% of Co (II) was extracted, while only 3.3% Ni(II) was extracted. The separation factor for Co(II)/Ni(II) was 3971. In the corresponding aqueous solvent extraction system, 99.0% Co(II) was extracted at 5.0 M LiCl while

15.6% Ni(II) was co-extracted. The separation factor of Co(II)/Ni(II) was 543 in this case, which is much smaller than that from the EG system. In addition to good separations of Zn(II)/Eu(III), Fe(III)/Nd(III) and Co(II)/Sm(III), the non-aqueous solvent extraction system involving EG is useful for the separation of Co(II) and Ni(II). The separation of Ni(II)/La(II) will be further investigated in another solvent extraction system.

Rare-earth elements could neither be extracted by Aliquat 336 through formation of an anionic complex with chloride ions, nor by the salting-out effect in polar organic solvents. Therefore, in principle, any metal ion that can form an anionic complex with chloride ions can be effectively separated from the rare earths by non-aqueous solvent extraction from EG solutions with Aliquat 336.

4. Conclusions

A non-aqueous solvent extraction system with the basic extractant Aliquat 336 in toluene as the less polar phase and ethylene glycol (+ LiCl) as the more polar phase was developed for the separation of Co(II) and Sm(III) as part of a recycling scheme for SmCo magnets. Co(II) could be extracted more efficiently from the EG solution than from the aqueous solutions. Sm(III) was not extracted at all from the EG solution, while it could be extracted to a large extent from the aqueous solution. As a result, Co(II) and Sm(III) could be separated completely in one single solvent extraction step using the developed non-aqueous solvent extraction system. In both the aqueous and the non-aqueous solvent extraction systems, Co(II) was extracted as the $[CoCl_4]^{2-}$ complex by an anion exchange mechanism. Sm(III) was extracted by the salting-out effect of LiCl in the aqueous system, but it was not extracted in the non-aqueous system because the salting-out effect of LiCl is much weaker in the EG solution. The salting-out effect revealed and the non-aqueous solvent extraction system developed in this study is transferrable to the separations of the metals pairs of Zn(II)/Eu(III) and Fe(III)/Nd(III).

Acknowledgement

The research was supported by the European Research Council (ERC) under the European Union's Horizon 2020 Research and Innovation Programme: Grant Agreement 694078 — Solvometallurgy for critical metals (SOLCRIMET). SR thanks the FWO Flanders for a PhD fellowship. Dr. Nagaphani Kumar Batchu is acknowledged for helpful discussions.

Conflict of interest

There are no conflicts of interest to declare.

References

[1] J. Rydberg, M. Cox, C. Musikas, G.R. Choppin, Solvent extraction principles and practice, second ed., Marcel Dekker Inc, New York, Basel, 2004.
[2] J.M. Perera, G.W. Stevens, The role of additives in metal extraction in oil/water systems, Solvent Extr. Ion Exch. 29 (3) (2011) 363–383.
[3] J.M. Sørensen, W. Arlt, Liquid-liquid equilibrium data collection-ternary systems, Frankfurt, DECHEMA, 1980.
[4] J.M. Sørensen, W. Arlt, Liquid-liquid equilibrium data collection-ternary and quaternary systems, Frankfurt, DECHEMA, 1980.
[5] Z. Li, K.H. Smith, K.A. Mumford, Y. Wang, G.W. Stevens, Regression of NRTL parameters from ternary liquid–liquid equilibria using particle swarm optimization and discussions, Fluid Phase Equilib. 398 (2015) 36–45.
[6] Z. Li, K.A. Mumford, K.H. Smith, J. Chen, Y. Wang, G.W. Stevens, Solution structure of isoactivity equations for liquid-liquid equilibrium calculations using the non-random two-liquid model, Ind. Eng. Chem. Res. 55 (10) (2016) 2852–2859.
[7] M.L. Michelsen, The isothermal flash problem, Part I. Stability. Fluid Phase Equilib. 9 (1) (1982) 1–19.
[8] M.L. Michelsen, The isothermal flash problem. Part II. Phase-split calculation, Fluid Phase Equilib. 9 (1) (1982) 21–40.
[9] E.M. Larsen, L.V.E. Trevorrow, The systems formed by zirconium and hafnium tetrachloride with acetonitrile and isoamyl ether, J. Inorg. Nucl. Chem. 2 (4) (1956) 254–259.
[10] G.W. Latimer, Distribution of Ion pairs between immiscible nonaqueous solvents, Anal. Chem. 35 (12) (1963) 1983-1983.
[11] T.M. Florence, Y.J. Farrar, Liquid-liquid extraction of nickel with long-chain amines from aqueous and nonaqueous halide media, Anal. Chem. 40 (8) (1968) 1200–1206.
[12] T. Florence, Y. Farrar, Liquid-liquid extraction of manganese, chromium, and thorium by long-chain amines from concentrated halide media, Aust. J. Chem. 22 (2) (1969) 473–476.
[13] A.R. Burns, R.W. Cattrall, The distribution of copper(II) between methanolic lithium chloride solutions and benzene solutions of bis(3,5,5-trimethylhexyl)ammonium chloride, J. Inorg. Nucl. Chem. 35 (7) (1973) 2489–2496.
[14] M. Matsui, T. Aoki, O. Inoue, T. Shigematsu, Nonaqueous liquid-liquid extraction. Extraction of zinc and cadmium from ethylene glycol solution of bromide by trioctylphosphine oxide, Bull. Inst. Chem. Res., Kyoto Univ. 52 (5–6) (1975) 652–657.
[15] M. Matsui, T. Aoki, H. Enomoto, T. Shigematsu, Nonaqueous liquid-liquid extraction: Extraction of zinc from ethylene glycol solution of chloride by trioctylphosphine oxide, Anal. Lett. 8 (4) (1975) 247–255.
[16] M. Matsui, H. Doe, T. Hirade, T. Shigematsu, Nonaqueous liquid-liquid extraction. Extraction of zinc from methanol-water solution of chloride by trioctylphosphine oxide in decaline, Anal. Lett. 12 (13) (1979) 1385–1397.
[17] N.K. Batchu, T. Vander Hoogerstraete, D. Banerjee, K. Binnemans, Non-aqueous solvent extraction of rare-earth nitrates from ethylene glycol to n-dodecane by Cyanex 923, Sep. Purif. Technol. 174 (2017) 544–553.
[18] N.K. Batchu, T. Vander Hoogerstraete, D. Banerjee, K. Binnemans, Separation of rare-earth ions from ethylene glycol (+LiCl) solutions by non-aqueous solvent extraction with Cyanex 923, RSC Adv. 7 (72) (2017) 45351–45362.
[19] S. Riano, M. Petranikova, B. Onghena, T. Vander Hoogerstraete, D. Banerjee, M.R.S. Foreman, C. Ekberg, K. Binnemans, Separation of rare earths and other valuable metals from deep-eutectic solvents: a new alternative for the recycling of used NdFeB magnets, RSC Adv. 7 (51) (2017) 32100–32113.
[20] M.R.S. Foreman, Progress towards a process for the recycling of nickel metal hydride electric cells using a deep eutectic solvent, Cogent Chem. 2 (1) (2016) 1139289.
[21] K. Binnemans, P.T. Jones, Solvometallurgy: an emerging branch of extractive metallurgy, J. Sustain. Metall. 3 (3) (2017) 570–600.
[22] K. Binnemans, P.T. Jones, B. Blanpain, T. Van Gerven, Y. Yang, A. Walton, M. Buchert, Recycling of rare earths: a critical review, J. Clean. Prod. 51 (2013) 1–22.
[23] Y. Yang, A. Walton, R. Sheridan, K. Güth, R. Gauß, O. Gutfleisch, M. Buchert, B.-M. Steenari, T. Van Gerven, P.T. Jones, K. Binnemans, REE recovery from end-of-life NdFeB permanent magnet scrap: a critical review, J. Sustain. Metall. 3 (1) (2017) 122–149.
[24] C. Deferm, M. Van de Voorde, J. Luyten, H. Oosterhof, J. Fransaer, K. Binnemans, Purification of indium by solvent extraction with undiluted ionic liquids, Green Chem. 18 (14) (2016) 4116–4127.
[25] T. Vander Hoogerstraete, S. Wellens, K. Verachtert, K. Binnemans, Removal of transition metals from rare earths by solvent extraction with an undiluted phosphonium ionic liquid: separations relevant to rare-earth magnet recycling, Green Chem. 15 (4) (2013) 919–927.
[26] L. Cui, F. Cheng, J. Zhou, Preparation of high purity $AlCl_3{\cdot}6H_2O$ crystals from coal mining waste based on iron(III) removal using undiluted ionic liquids, Sep. Purif. Technol. 167 (2016) 45–54.
[27] G. Zhang, D. Chen, W. Zhao, H. Zhao, L. Wang, D. Li, T. Qi, A novel synergistic extraction method for recovering vanadium (V) from high-acidity chloride leaching liquor, Sep. Purif. Technol. 165 (2016) 166–172.
[28] J.Y. Lee, B. Raju, B.N. Kumar, J.R. Kumar, H.K. Park, B.R. Reddy, Solvent extraction separation and recovery of palladium and platinum from chloride leach liquors of spent automobile catalyst, Sep. Purif. Technol. 73 (2) (2010) 213–218.
[29] K. Larsson, K. Binnemans, Separation of rare earths by split-anion extraction, Hydrometallurgy 156 (2015) 206–214.
[30] S. Riaño, M. Regadío, K. Binnemans, T. Vander Hoogerstraete, Practical guidelines for best practice on total reflection X-ray fluorescence spectroscopy: analysis of aqueous solutions, Spectrochim. Acta B. 124 (2016) 109–115.
[31] M. Regadío, S. Riaño, K. Binnemans, T. Vander Hoogerstraete, Direct analysis of metal ions in solutions with high salt concentrations by total reflection X-ray fluorescence, Anal. Chem. 89 (8) (2017) 4595–4603.
[32] A.O. Gorbunov, N.A. Tsyrul'nikov, A.A. Tikhomirova, N.A. Bogachev, M.Y. Skripkin, A.B. Nikolskii, O.N. Pestova, Solubility of d-element salts in organic and aqueous–organic solvents: II. Effect of halocomplex formation on solubility of cobalt bromide and chloride and nickel chloride, Russ. J. Gen. Chem. 86 (2016) 771–777.
[33] T. Mioduski, C. Gumiński, D. Zeng, IUPAC-NIST solubility data series. 87. Rare earth metal chlorides in water and aqueous systems. Part 2. Light lanthanides (Ce–Eu), J. Phys. Chem. Ref. Data 38 (2009) 441–562.
[34] T. Mioduski, M. Salomon, Scandium, yttrium, lanthanum and lanthanide halides in nonaqueous solvents, Pergamon, Oxford, 1985.
[35] Hafiz-ur-Rehman, M. Shahid Ansari, Density, viscosity, and electrical conductivity measurements on the ternary system H_2O + C_2H_5OH + LiCl over the entire ranges of solvent composition and LiCl solubility from (−5 to +50) °C, J. Chem. Eng. Data 53 (2008) 2072–2088.
[36] T. Sato, T. Shimomura, S. Murakami, T. Maeda, T. Nakamura, Liquid-liquid extraction of divalent manganese, cobalt, copper, zinc and cadmium from aqueous chloride solutions by tricaprylmethylammonium chloride, Hydrometallurgy 12 (2) (1984) 245–254.
[37] S.S. Foltova, T. Vander Hoogerstraete, K. Binnemans, Samarium/cobalt separation by solvent extraction with ionic liquids, in: Oral presentation at the 2nd European

Rare Earth Resources Conference, Santorini (Greece), 28-30 May 2017.
[38] F.G. Seeley, D.J. Crouse, Extraction of Metals from Chloride Solutions and Amines, J. Chem. Eng. Data. 11 (3) (1966) 424–429.
[39] M. Zahn, Y. Ohki, D.B. Fenneman, R.J. Gripshover, V.H. Gehman, Dielectric properties of water and water/ethylene glycol mixtures for use in pulsed power system design, Proc. IEEE. 74 (9) (1986) 1182–1221.
[40] G. Stanescu, A. Trutia, On absorption spectra of $CoCl_2$/acetone systems, J. Optoelectron. Adv. Mater. 7 (2) (2005) 1009–1015.
[41] C.M. Grgicak, R.G. Green, J.B. Giorgi, Control of microstructure, sinterability and performance in Co-precipitated NiYSZ, CuYSZ and CoYSZ SOFC anodes, J. Mater. Chem. 16 (9) (2006) 885–897.
[42] H. Yamamoto, M. Morishita, Y. Mizuta, A. Masubuchi, Electrodeposition of Co–Sb thermoelectric film from ethylene glycol–$CoCl_2$–$SbCl_3$ solution, Surf. Coat. Technol. 206 (15) (2012) 3415–3420.
[43] W. Simka, D. Puszczyk, G. Nawrat, Electrodeposition of metals from non-aqueous solutions, Electrochim. Acta 54 (23) (2009) 5307–5319.
[44] C.A. Morais, V.S.T. Ciminelli, Recovery of europium by chemical reduction of a commercial solution of europium and Gadolinium chlorides, Hydrometallurgy 60 (3) (2001) 247–253.